

**UNITED STATES PATENT APPLICATION**  
**FOR**  
**RESHAPABLE HAIR STYLING RINSE COMPOSITION**  
**COMPRISING (METH)ACRYLIC COPOLYMERS**  
**BY**  
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[001] The present invention relates to a reshapable hair styling composition. In particular, the present invention relates to a reshapable hair styling composition that is a rinse composition.

[002] Fixing the hairstyle is an important element in hair styling, and involves maintaining a shaping that has already been carried out. In accordance with the invention, the term "hair styling composition" relates to any kind of hair composition that can be used to effect hair styling.

[003] The most prevalent hair styling compositions on the cosmetic market for shaping and/or maintaining the hairstyle are spray compositions comprising a solution, usually alcohol- or water-based, and one or more materials, generally polymer resins. One of the functions of polymer resins is to form links between the hairs. These materials, also called fixatives, are often found in a mixture with various cosmetic adjuvants. This solution is generally packaged either in an appropriate aerosol container, which is pressurized with the aid of a propellant, or in a pump flask.

[004] Many hair styling compositions exist that have the same disadvantage: they are not designed to allow the hairstyle to be later modified to a desired shape, which is other than that formed initially, without starting the styling and fixing operations again. Moreover, under various kinds of stress, the hairstyle has a tendency to take on an undesirable permanent set, which cannot easily be modified. Also in the styling process, one may desire hair conditioning benefits, such as ease of combing and soft hair feel appearance.

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[005] A subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) units derived from at least one monomer chosen from butyl (meth)acrylate monomers, (b) units derived from at least one monomer chosen from hydroxy alkyl (meth)acrylate monomers, and (c) optional units derived from at least one co-polymerizable monomer other than said (a) and (b) monomers, wherein said composition provides a reshapable effect and is a rinse composition, with the proviso that (meth)acrylic copolymers derived from a 65/15/20 or a 75/15/10 weight percent ratio of n-butylacrylate/2-hydroxyethylacrylate/methylmethacrylate are excluded.

[006] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 10 to about 90 weight percent of units derived from at least one monomer chosen from butyl (meth)acrylate monomers, (b) from about 2 to about 50 weight percent of units derived from at least one monomer chosen from hydroxy alkyl (meth)acrylate monomers, and (c) optional units derived from at least one co-polymerizable monomer other than said (a) and (b) monomers, wherein said composition provides a reshapable effect and is a rinse composition, with the proviso that (meth)acrylic copolymers derived from a 65/15/20 or a 75/15/10 weight percent ratio of n-butylacrylate/2-hydroxyethylacrylate/methylmethacrylate are excluded.

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[007] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 10 to about 90 weight percent of units derived from at least one monomer chosen from n-butyl (meth)acrylate monomers, (b) from about 2 to about 50 weight percent of units derived from at least one monomer chosen from 2-hydroxy ethyl (meth)acrylate monomers, and (c) up to about 80 weight percent of units derived from at least one monomer chosen from 2-ethyl hexyl (meth)acrylate monomers, wherein said composition provides a reshapable effect and is a rinse composition, with the proviso that (meth)acrylic copolymers derived from a 65/15/20 or a 75/15/10 weight percent ratio of n-butylacrylate/2-hydroxyethylacrylate/methylmethacrylate are excluded.

[008] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 30 to about 40 weight percent of units derived from at least one monomer chosen from n-butyl acrylate monomers, (b) from about 2 to about 10 weight percent of units derived from at least one monomer chosen from 2-hydroxy ethyl methacrylate monomers, and (c) from about 50 to about 70 weight percent of units derived from at least one monomer chosen from 2-ethyl hexyl acrylate monomers, wherein said composition provides a reshapable effect and is a rinse composition.

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[009] A further subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, (1) at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) units derived from at least one monomer chosen from butyl (meth)acrylate monomers, (b) units derived from at least one monomer chosen from hydroxy alkyl (meth)acrylate monomers, and (c) optional units derived from at least one co-polymerizable monomer other than said (a) and (b) monomers, and (2) at least one surfactant, wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[010] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, (1) at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) units derived from at least one monomer chosen from butyl (meth)acrylate monomers, (b) units derived from at least one monomer chosen from hydroxy alkyl (meth)acrylate monomers, and (c) optional units derived from at least one co-polymerizable monomer other than said (a) and (b) monomers, and (2) at least one conditioning agent, wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[011] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, (1) at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 10 to about 90 weight percent of units derived from at least one monomer chosen from butyl (meth)acrylate monomers, (b) from about 2 to

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about 50 weight percent of units derived from at least one monomer chosen from hydroxy alkyl (meth)acrylate monomers, and (c) optional units derived from at least one co-polymerizable monomer other than said (a) and (b) monomers, and (2) at least one surfactant, wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[012] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, (1) at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 10 to about 90 weight percent of units derived from at least one monomer chosen from butyl (meth)acrylate monomers, (b) from about 2 to about 50 weight percent of units derived from at least one monomer chosen from hydroxy alkyl (meth)acrylate monomers, and (c) optional units derived from at least one co-polymerizable monomer other than said (a) and (b) monomers, and (2) at least one conditioning agent, wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[013] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, (1) at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 10 to about 90 weight percent of units derived from at least one monomer chosen from n-butyl (meth)acrylate monomers, (b) from about 2 to about 50 weight percent of units derived from at least one monomer chosen from 2-hydroxy ethyl (meth)acrylate monomers, and (c) up to about 80 weight percent of units derived from at least one monomer chosen from 2-ethyl hexyl (meth)acrylate

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wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[016] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, (1) at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 30 to about 40 weight percent of units derived from at least one monomer chosen from n-butyl acrylate monomers, (b) from about 2 to about 10 weight percent of units derived from at least one monomer chosen from 2-hydroxy ethyl methacrylate monomers, and (c) from about 50 to about 70 weight percent of units derived from at least one monomer chosen from 2-ethyl hexyl acrylate monomers, and (2) at least one surfactant, wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[017] Another subject of the invention is a reshapable hair styling composition comprising, optionally in a cosmetically acceptable vehicle, (1) at least one (meth)acrylic copolymer, wherein the at least one (meth)acrylic copolymer comprises: (a) from about 30 to about 40 weight percent of units derived from at least one monomer chosen from n-butyl acrylate monomers, (b) from about 2 to about 10 weight percent of units derived from at least one monomer chosen from 2-hydroxy ethyl methacrylate monomers, and (c) from about 50 to about 70 weight percent of units derived from at least one monomer chosen from 2-ethyl hexyl acrylate monomers, and (2) at least one conditioning agent, wherein said

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composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[018] The weight percentages of the (a), (b), and (c) units is based on the total weight of each monomer type used compared to the total weight of all monomers used.

[019] Another subject of the invention is a reshapable hair styling composition comprising at least one (meth)acrylic copolymer, as described above, wherein said reshapable hair styling composition is a rinse composition, including, for example shampoos and conditioners, in the form of a spray, aerosol, mousse, gel, lotion, cream, dispersion, or emulsion.

[020] Another subject of the invention is an aerosol device comprising a vessel, which comprises: (1) an aerosol composition, which provides a reshapable effect and comprises a liquid phase comprising at least one composition comprising at least one (meth)acrylic copolymer, as described above, wherein said composition is a rinse composition, including, for example shampoos and conditioners, and a propellant, and (2) a dispenser.

[021] Another subject of the invention is a method of cosmetically treating hair, comprising applying to the hair before shaping of a hairstyle of said hair a composition comprising at least one (meth)acrylic copolymer, as described above, wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners.

[022] Another subject of the invention is a method of reshaping hair, comprising: (1) applying to the hair before the initial shaping of the hairstyle a

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composition comprising at least one (meth)acrylic copolymer, as described above, wherein said composition provides a reshapable effect and is a rinse composition, including, for example shampoos and conditioners, and (2) thereafter shaping the hairstyle at least once, wherein no additional composition or heat is needed.

[023] Another subject of the invention is a method of manufacturing a reshapable hair styling composition comprising including in a hair styling composition at least one (meth)acrylic copolymer, as described above, wherein said at least one (meth)acrylic copolymer is present in an amount effective to provide a reshapable effect and said composition is a rinse composition, including, for example shampoos and conditioners.

[024] The term “(meth)acrylate” is used to encompass both the terms acrylate and methacrylate. Similarly, the term “(meth)acrylic acid” is used to encompass both acrylic acid and methacrylic acid. As used herein, the term “polyfunctional crosslinking agent” is used to mean a crosslinking agent having an average functionality greater than 1, such as greater than 1.8, and further such as about 2.0 or greater. But the average functionality is less than about 6, such as less than about 4, and further such as about 3 or less. The term “rinse composition” is used to mean any composition that is formulated to be rinsed off after application to the hair.

[025] The rinse composition may be in any of the conventional forms of rinse cosmetic compositions including, but not limited to, shampoos, conditioners, hair rinses, permanent waving compositions, waving compositions, hair dye compositions, products to use before or after a hair dye treatment, products to use

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before or after a permanent waving treatment, hair straightening compositions, products to use before or after a hair straightening treatment, and combinations thereof. A shampoo has a cleansing effect upon the hair and may also have a conditioning effect. A conditioner has a conditioning effect upon the hair without a cleansing effect.

[026] The term "reshapable" hair styling composition means a hair styling composition providing hair styling that can be restored or modified without new material or heat being applied. For example, in order to restore or modify the hairstyle in case of "drooping" or loss of setting (dishevelment), no new materials, such as water or any form of fixing agent, or heat are required. Thus, to provide a "reshapable" effect means to provide a hair styling that can be restored or modified without new material or heat being applied. The efficacy of the composition can be long lasting, such as 10-24 hours, giving rise to a durable styling effect. Other terms, which may be synonymous with reshapable, include repositionable, remoldable, restyleable, rearrangeable, and remodelable.

[027] In one embodiment of the invention, the (meth)acrylic copolymer of such reshapable hair styling compositions may be in the form of an emulsion or dispersion. All emulsions comprise a continuous phase and at least one dispersed phase. The term "dispersion" means generally a multi-phase system where at least one phase contains discrete particles distributed throughout a bulk substance. A portion of the polymer may exist as the discrete particle in an aqueous phase. Dispersions are possible through the use of certain components that are insoluble in the aqueous system. By "dispersion," it is also meant that not necessarily the entire

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[029] In general, the monomers recited in (a) constitute, for example, from about 10 to about 90 weight percent of the total amount of monomers used. In one embodiment, they may constitute from about 15 to about 50 weight percent of the total amount of monomers used. In a separate embodiment, they may constitute from about 50 to about 90 weight percent of the total amount of monomers used, such as from about 70 to about 90 weight percent of the total amount of monomers used. The monomers recited in (a) are butyl (meth)acrylate monomers such as, for example, n-butyl (meth)acrylate, t-butyl (meth)acrylate, isobutyl (meth)acrylate, 2-decylbutyl (meth)acrylate, and 2-methylbutyl (meth)acrylate. In one embodiment, the monomers recited in (a) are selected from n-butyl acrylate.

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embodiment, they may constitute from about 2 to about 25 weight percent of the total amount of monomers used. In a separate embodiment, they may constitute from about 10 to about 50 weight percent of the total amount of monomers used, such as from about 10 to about 30 weight percent of the total amount of monomers used. The monomers recited in (b) are hydroxy alkyl (meth)acrylate monomers such as, for example, 2-hydroxy ethyl (meth)acrylate, hydroxy propyl (meth)acrylate, 2,3-dihydroxy propyl (meth)acrylate, 4-hydroxy butyl (meth)acrylate, and 2-hydroxy propyl (meth)acrylate. In one embodiment, the monomers recited in (b) are selected from 2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate, and hydroxy propyl acrylate monomers.

[031] In general, the optional monomers recited in (c) constitute for example, up to about 80 weight percent of the total amount of monomers used. In one embodiment, they may constitute from about 30 to about 80 weight percent of the total amount of monomers used. In a separate embodiment, they may constitute up to about 50 weight percent of the total amount of monomers used, such as up to about 30 weight percent of the total amount of monomers used. The optional at least one co-polymerizable monomer recited in (c) may be chosen from (i) alkyl(meth)acrylate monomers, (ii) polar monomers and (iii) ethylenically unsaturated free radically polymerizable monomers. Alkyl(meth)acrylate monomers may include, for example, methyl (meth)acrylate, isobornyl (meth)acrylate, ethyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, lauryl (meth)acrylate, octa decyl (meth)acrylate, and mixtures thereof. In another embodiment, the units derived from 2-ethyl hexyl (meth)acrylate monomers constitute from about 30 to

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about 80 weight percent of the total amount of monomers used. Useful polar monomers include (meth)acrylic acid, itaconic acid, N-vinyl pyrrolidone, N-vinyl caprolactam, substituted (meth)acrylamides (such as N,N,-dimethyl (meth)acrylamides and N-octyl (meth)acrylamide), dimethylaminoethyl (meth)acrylate, (meth)acrylonitrile, 2-carboxyethyl (meth)acrylate, maleic anhydride, and mixtures thereof. Another example of useful polar monomers is methoxypolyethylene glycol 550 monoacrylate available from Sartomer Co. under the tradename CD553. Useful ethylenically unsaturated free radically polymerizable monomers include styrene and C<sub>1</sub>-C<sub>4</sub> vinyl esters such as vinyl acetate, vinyl propionate, and mixtures thereof. In yet another embodiment, the units derived from the co-polymerizable ethylenically unsaturated free radically polymerizable monomers are present in the range up to about 30% by weight.

[032] One or more polyfunctional crosslinking agents may be included. Examples of crosslinking agents include but are not limited to those chosen from divinylbenzene, alkyl diacrylates (such as those chosen from 1,2-ethylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, 1,8-octanediol diacrylate, and 1,12-dodecanediol diacrylate), alkyl triacrylates and alky tetracrylates (such as trimethylol propane triacrylate and pentaerythritol tetraacrylate), monoethylenically unsaturated aromatic ketones (such as 4-acryloxybenzophenone), multifunctional aziridine amides (such as 1,1'-(1,3-phenylenedicarbonyl)bis[2-methyl aziridine], 2,2,4-trimethyladipoyl bis [2-ethyl aziridine], 1, 1'-azelaoyl bis [2-methyl aziridine], and 2,4,6-tris(2-ethyl-1-aziridinyl)-1,3,5 triazine), metal ion crosslinkers (such as copper,

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zinc, zirconium, and chromium) and mixtures thereof. In one embodiment, the metal ion crosslinkers are chosen from chelated esters of ortho-titanic acid sold under the tradename TYZOR and commercially available from the E.I. du Pont de Numours Co. In another embodiment, the TYZOR is TYZOR AA, which is titanium acetyl acetate. In yet another embodiment, the crosslinking agent is 1,6-hexanediol diacrylate.

[033] Crosslinking agents, when used, comprise up to about 10 parts by weight, typically about 0.1 to about 2 parts by weight of the total copolymerizable mixture based on 100 parts by weight of the monomers recited in (a), (b), and (c), when present.

[034] In one embodiment, the copolymer may be optionally obtained with one or more water-soluble and/or oil-soluble initiators, which are useful in preparing (meth)acrylic emulsions. Such initiators, on exposure to heat, generate free-radicals which initiate (co)polymerization of the butyl (meth)acrylate monomers, hydroxyalkyl (meth)acrylate monomers, and the optional comonomer and crosslinking agent components. In one embodiment, one or more water soluble initiators are used. Suitable water-soluble initiators include but are not limited to those chosen from potassium persulfate, ammonium persulfate, sodium persulfate, and mixtures thereof; oxidation-reduction initiators such as the reaction product of the above-mentioned persulfates and reducing agents such as those chosen from sodium metabisulfite and sodium bisulfite; and 4,4'-azobis(4-cyanopentanoic acid) and its soluble salts (e.g., sodium, potassium). In another embodiment, the water-soluble initiator is potassium persulfate.

[035] Suitable oil-soluble initiators include but are not limited to those chosen from azo compounds such as VAZO 64 (2,2'-azobis(isobutyronitrile) and VAZO 52 (2,2'-azobis(2,4-dimethylpentanenitrile)), both available from E.I. du Pont de Numours Co.; and peroxides such as benzoyl peroxide, lauroyl peroxide, and mixtures thereof. In one embodiment, the oil-soluble thermal initiator is 2,2'-azobis(isobutyronitrile). When used, initiator(s) may comprise from about 0.05 to about 1 parts by weight, also about 0.1 to about 0.5 parts by weight based on 100 parts by weight of the total copolymerizable mixture

[036] In another embodiment, the copolymer may be optionally obtained with one or more chain transfer agents. Examples of useful chain transfer agents include but are not limited to those chosen from carbon tetrabromide, alcohols, mercaptans, and mixtures thereof. In one embodiment, the chain transfer agent is chosen from isooctylthioglycolate and carbon tetrabromide. The copolymerizable mixture may further comprise up to about 0.5 parts by weight of one or more chain transfer agents, typically about 0.01 weight percent to about 0.5 parts by weight, if used, also about 0.05 parts by weight to about 0.2 parts by weight, based upon 100 parts by weight of the total copolymerizable mixture.

[037] Polymerization via emulsion techniques may require the presence of one or more emulsifiers (which may also be called emulsifying agents or surfactants). Useful emulsifiers for the present invention include those chosen from anionic surfactants, nonionic surfactants, and mixtures thereof.

[038] Useful anionic surfactants, as emulsifiers, include but are not limited to those whose molecular structure includes at least one hydrophobic moiety chosen

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[039] Useful nonionic surfactants, as emulsifiers, include but are not limited to those whose molecular structure comprises a condensation product of an organic aliphatic and/or alkyl aromatic hydrophobic moiety with a hydrophilic alkylene oxide such as ethylene oxide. The HLB (Hydrophilic-Lipophilic Balance) of useful nonionic surfactants, as emulsifiers, is about 10 or greater, such as from about 10 to about 20. The HLB of a surfactant is an expression of the balance of the size and strength of the hydrophilic (water-loving or polar) groups and the lipophilic (oil-loving or non-polar) groups of the surfactant. Commercial examples of nonionic surfactants useful in the present invention include but are not limited to nonylphenoxy or octylphenoxy poly(ethyleneoxy) ethanols available from Rhône-Poulenc as the IGEPAL CA or CO series, respectively; C<sub>11</sub>-C<sub>15</sub> secondary-alcohol ethoxylates available from Union Carbide as the TERGITOL 15-S series; and polyoxyethylene

sorbitan fatty acid esters available from ICI Chemicals as the TWEEN series of surfactants.

[040] In one embodiment, an emulsion polymerization of this invention is carried out in the presence of one or more anionic surfactants, as emulsifiers. A useful range of emulsifier concentration is from about 0.5 to about 8 weight percent, such as from about 1 to about 5 weight percent, based on the total weight of all monomers.

[041] In one embodiment, the (meth)acrylic copolymers are (meth)acrylic emulsions or dispersions. (Meth)acrylic emulsions and dispersions may be prepared by a semi-continuous emulsion polymerization process. In the process, a flask is charged with a seed monomer mixture comprising deionized (DI) water, surfactant, butyl (meth)acrylate monomers recited in (a), hydroxyalkyl (meth)acrylate monomers recited in (b), and the optional components such as co-polymerizable monomers recited in (c), polyfunctional crosslinking agents, chain transfer agents, pH modifiers, and other additives. The mixture is stirred and heated under an inert atmosphere such as a nitrogen blanket. When the mixture has reached induction temperature, typically about 50 °C to about 70 °C, the first initiator is added to initiate the polymerization and the reaction is allowed to exotherm. After the seed reaction is completed, the batch temperature is then raised to the feed reaction temperature, about 70 °C to about 85 °C. At the feed reaction temperature, the monomer pre-emulsion comprising DI water, surfactant, butyl (meth)acrylate monomers recited in (a), hydroxyalkyl (meth)acrylate monomers recited in (b), and the optional components such as co-polymerizable monomers recited in (c), polyfunctional

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crosslinking agents, chain transfer agents, and other additives is added to the stirred flask over a period of time, typically 2 to 4 hours, while the temperature is maintained. At the end of the feed reaction, the second initiator charge, if used, is added to the reaction to further reduce residual monomers in the emulsion/dispersion. After an additional hour of heating, the mixture is cooled to room temperature (about 23 °C) and the emulsion/dispersion is collected for evaluation.

[042] In one embodiment, the pH of the emulsion/dispersion prepared using this method is about 2 to about 3. The acidity of the emulsion/dispersion can be modified following emulsion/dispersion formation using one or more pH modifiers such as a basic solutions (e.g., solutions of sodium hydroxide, ammonium hydroxide and the like) or buffer solutions (e.g., sodium bicarbonate and the like), to less acidic levels. In another embodiment, the pH is 7 or less. In yet another embodiment, the pH is in the range of 2 to 6.

[043] In one embodiment of the invention, the (meth)acrylic copolymers may be neutralized in the emulsion/dispersion and/or in the composition by one or more neutralizing agents. Suitable neutralizing agents may be chosen from organic, inorganic, and organomineral bases, such as amino methyl propanols, sodium and potassium hydroxides, primary, secondary and tertiary amines, ammoniacs, derivatives thereof, and combinations thereof.

[044] In one embodiment, the (meth)acrylic emulsions of the invention may also contain one or more conventional additives, such as plasticizers, dyes, fillers,

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antioxidants, and UV stabilizers. Such additives can be used if they do not adversely affect the reshapable properties of the composition.

[045] In yet another embodiment of the invention, the (meth)acrylic copolymer has a glass transition temperature (T<sub>g</sub>) ranging from about -100 °C to about 15 °C. According to the present invention, the T<sub>g</sub> of the (meth)acrylic copolymer is obtained following the application of the (meth)acrylic copolymer in a aqueous or hydroalcoholic medium to a matrix and then drying until the weight does not change. The glass transition temperature is determined by the Differential Scanning Calorimetric method (DSC).

[046] In one embodiment of the invention, the (meth)acrylic copolymer is chosen from nonionic and weakly anionic (meth)acrylic copolymers. Weakly anionic means that the level of units derived from anionic monomers in the copolymer is less than about 5% by weight.

[047] In one embodiment of the invention, the (meth)acrylic copolymer may be present in an amount ranging from about 0.01 to about 40, such as from about 0.1 to about 15, weight percent of the total weight of the composition in order to provide a reshapable effect.

[048] The composition may further comprise any cosmetically acceptable vehicle that does not substantially interfere with the adhesive properties of the at least one (meth)acrylic copolymer. The choice of vehicle is adapted to the method of application selected. In one embodiment, the cosmetically acceptable vehicle may be chosen from water, water miscible solvents such as lower alcohols, e.g., C<sub>1</sub> to C<sub>4</sub> branched and straight chain aliphatic alcohols, and combinations thereof. In

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one embodiment, the at least one adhesive particle is insoluble in the cosmetically acceptable vehicle.

[049] The vehicle may also comprise one or more additional solvents. For example, other rapid evaporating solvents may be used, such as hexamethyldisiloxane (HMDS); cyclic silicones (D<sub>4</sub> and D<sub>5</sub>); C<sub>4</sub>-C<sub>10</sub> alkanes including isoparaffins such as Permethyl 97A and Isopar C; acetone; hydrofluoroethers (HFEs) and the like.

[050] The composition according to the invention may further comprise at least one constituent known in the cosmetic arts that does not substantially interfere with the reshaping properties of the at least one (meth)acrylic copolymer. Such constituents may be chosen from, but are not limited to: reducing agents (such as thiols); silanes (such as aminopropyl triethoxy silane); fatty substances; thickeners; plasticizers; anti-foaming agents; hydrating agents; fillers; sunscreens (such as UV filters); active haircare agents; perfumes; preservatives; cationic, anionic, nonionic, and amphoteric (such as zwitterionic) surfactants; cationic, anionic, nonionic, and amphoteric (such as zwitterionic) polymers other than polymers of the invention; polyols; proteins; provitamins; vitamins; dyes; tints; bleaches; and pH adjusting agents. The compositions may also contain a conditioning agent such as, for example, such as silicones, fatty esters, fatty alcohols, long chain hydrocarbons, emollients, lubricants, polymers, surfactants, lanolin compounds, ceramides, proteins, protein hydrolysates, and other protein derivatives. As used herein, the term "conditioning agent" means any agent whose function is to improve the cosmetic properties of the hair, for example, the softness, ease of disentangling,

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feel, and lack of static electricity. In one embodiment, the at least one conditioning agent is chosen from cationic surfactants, cationic polymers, and silicones.

[051] In one embodiment, the at least one constituent is chosen from polymers, such as anionic, cationic, amphoteric (such as zwitterionic), and nonionic polymers and combinations thereof. As used herein, the term "polymer" refers to homopolymers and copolymers, the copolymers being derived from more than one type of monomer, such as from two, three, four, or more different monomer types.

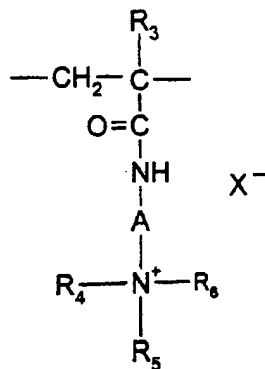
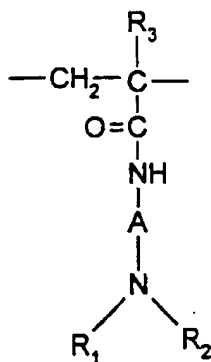
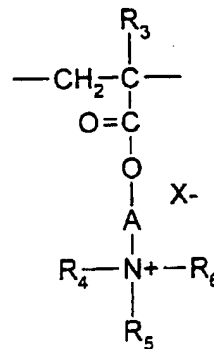
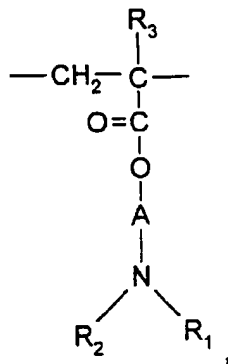
[052] The cationic polymers comprise cationic moieties or moieties that are convertible to cationic moieties. Suitable examples of cationic polymers, which can be used according to the present invention, are those that may be chosen from polymers comprising at least one group chosen from primary amine groups, secondary amine groups, tertiary amine groups, and quaternary amine groups, wherein the at least one group forms part of the polymer chain or is linked directly to it, having a weight average molecular weight ranging from about 500 to about 5,000,000, such as from about 1000 to about 3,000,000.

[053] Among these polymers, mention may be made more particularly of the following cationic conditioning polymers:

[054] (1) homopolymers and copolymers derived from monomers chosen from (meth)acrylic esters and (meth)acrylic amides comprising units of at least one of the following formulae:

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in which each  $\text{R}_3$  is independently chosen from hydrogen and  $\text{CH}_3$  groups; each A is independently chosen from linear and branched alkyl groups comprising 1 to 6 carbon atoms and hydroxyalkyl groups comprising 1 to 4 carbon atoms; each  $\text{R}_4$ ,  $\text{R}_5$ , and  $\text{R}_6$  is independently chosen from alkyl groups comprising 1 to 18 carbon atoms and benzyl groups; each  $\text{R}_1$  and  $\text{R}_2$  is independently chosen from hydrogen and alkyl groups comprising 1 to 6 carbon atoms; and each  $\text{X}^-$  is independently chosen from methyl sulfate anions and halide anions, such as chloride or bromide anions.

[055] In one embodiment, the copolymers of family (1) further comprise at least one unit derived from monomers chosen from (meth)acrylamides, diacetone (meth)acrylamides, (meth)acrylamides substituted on the nitrogen by a group chosen from lower alkyls, (meth)acrylic acids, esters of (meth)acrylic acids, vinyl lactams such as vinylpyrrolidone and vinyl-caprolactam, and vinyl esters.

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[056] Thus, mention may be made, among these cationic conditioning copolymers of the family (1), of:

- copolymers of acrylamide and of dimethylaminoethyl methacrylate quaternized with dimethyl sulfate or with a dimethyl halide, such as Hercofloc available from the company Hercules;
- copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium chloride which are disclosed, for example, in EP-A-080,976, the disclosure of which relating to cationic polymers is incorporated herein by reference, and sold, for example, under the name Bina Quat P 100 by the company Ciba-Geigy;
- copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium methosulfate, such as Reten available from the company Hercules;
- optionally quaternized vinylpyrrolidone/dialkyl-aminoalkyl (meth)acrylate copolymers, which are disclosed, for example, in French Patents 2,077,143 and 2,393,573, the disclosures of which relating to cationic polymers are incorporated herein by reference, and sold, for example, under the name "Gafquat" by the company ISP, such as, for example, "Gafquat 734" or "Gafquat 755", or else the products named "Copolymer 845, 958 and 937";
- dimethylaminoethyl methacrylate/vinylcaprolactam/vinylpyrrolidone terpolymers, such as the product sold under the name Gaffix VC 713 by the company ISP;
- vinylpyrrolidone/methacrylamidopropyl dimethylamine copolymers sold in particular under the name Styleze CC 10 by ISP, and
- the quaternized vinylpyrrolidone/dimethylamino-propylmethacrylamide copolymer, such as the product sold under the name "Gafquat HS 100" by the company ISP.

FOOTNOTES

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[059] The commercial products corresponding to this definition are more particularly the products sold under the name "Celquat L 200" and "Celquat H 100" by the company National Starch.

[061] Mention may be made, among these compounds, of the chitosan having a degree of deacetylation of 90.5% by weight sold under the name Kytan

Crude Standard by the company Aber Technologies and the chitosan pyrrolidone-carboxylate sold under the name Kytamer PC by the company Amerchol.

[062] (5) the quaternized polysaccharides, disclosed more particularly in U.S. Patent Nos. 3,589,578 and 4,031,307, the disclosures of which relating to quaternized polysaccharides polymers are incorporated herein by reference, such as guar gums comprising cationic trialkylammonium cationic groups. Examples include guar gums modified with a salt (e.g., chloride) of 2,3-epoxypropyltrimethyl ammonium.

[063] Such products are sold in particular under the trade names Jaguar C13 S, Jaguar C 15, Jaguar C 17, and Jaguar C162 by the company Meyhall.

[064] (6) copolymers comprising piperazinyl units and divalent alkylene and divalent hydroxyalkylene groups containing straight and branched chains, optionally interrupted by one or more oxygen atoms, sulfur atoms, nitrogen atoms, aromatic rings, and heterocyclic rings. Examples include the oxidation and quaternization products of these copolymers. Such polymers are described, in particular, in French patents 2,162,025 and 2,280,361, the disclosures of which relating to copolymers comprising piperazinyl units are incorporated herein by reference.

[065] (7) water-soluble polyamino amides, which may be prepared by polycondensation of an acidic compound with a polyamine. These polyamino amides can be crosslinked with at least one compound chosen from epihalohydrins, diepoxides, dianhydrides, unsaturated dianhydrides, bis-unsaturated derivatives, bis-halohydrins, bis-azetidiniums, bis-haloacyldiamines, bis-alkyl halides, and oligomers,

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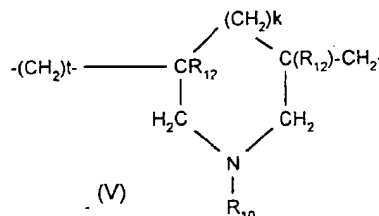
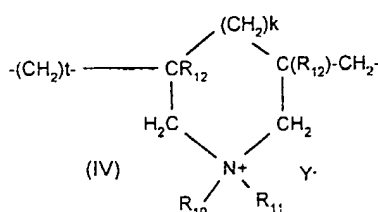
[066] (8) polyaminoamide derivatives resulting from the condensation of polyalkylene polyamines with polycarboxylic acids followed by alkylation with difunctional agents. Examples include adipic acid/ dialkylamino hydroxyalkyl dialkylenetriamine polymers, wherein the alkyl groups are C<sub>1</sub>-C<sub>4</sub> alkyl groups (such as methyl, ethyl, and propyl), such as adipic acid/dimethylamino hydroxypropyl diethylenetriamine polymers sold under the name "Cartaretine F, F4, and F8" by the company Sandoz. Such polymers are described in particular in French patent 1,583,363, the disclosure of which relating to polyaminoamide derivatives is incorporated herein by reference.

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1.4:1. The polyamino amide resulting therefrom is reacted with epichlorohydrin in a molar ratio of epichlorohydrin relative to the secondary amine group of the polyamino amide of between about 0.5:1 and about 1.8:1. Such polymers are described in particular in U.S. Patent Nos. 3,227,615 and 2,961,347, the disclosures of which relating to polymers obtained by reacting a polyalkylene polyamine with a dicarboxylic acid are incorporated herein by reference.

[068] Polymers of this type are sold in particular under the name "Hercosett 57" by the company Hercules Inc. or alternatively under the name "PD 170" or "Delsette 101" by the company Hercules in the case of the adipic acid/epoxypropyl/diethylenetriamine copolymer.

[069] (10) cyclopolymers of alkylallylamine and/or of dialkylallylammmonium, such as the homopolymers or copolymers containing, as main constituent of the chain, units chosen from formulae (IV) and/or (V):

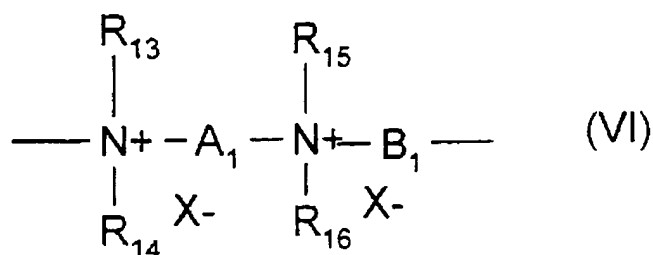


wherein k and t are either 0 or 1 and the sum k + t equals 1; each R<sub>12</sub> is independently chosen from hydrogen and methyl groups; R<sub>10</sub> and R<sub>11</sub>, are independently chosen from alkyl groups having from 1 to 8 carbon atoms (such as from 1 to 4 carbon atoms), C<sub>1</sub>-C<sub>5</sub> hydroxyalkyl groups, and C<sub>1</sub>-C<sub>4</sub> amidoalkyl groups, or R<sub>10</sub> and R<sub>11</sub>, together with the nitrogen atom to which they are attached, may form a heterocyclic group, such as piperidyl and morpholinyl; Y<sup>-</sup> is independently chosen from anions, such as bromide, chloride, acetate, borate, citrate, tartrate, bisulfate,

bisulfite, sulfate, and phosphate anions. These polymers are described in particular in French patent 2,080,759 and in its Certificate of Addition 2,190,406, the disclosures of which relating to cyclopolymers of alkyldiallylamine and/or of dialkyldiallylammonium are incorporated herein by reference.

[070] Among the polymers defined above, mention may be made more particularly of the dimethyldiallylammonium chloride homopolymer sold under the name "Merquat 100" by the company Calgon (its homologues of low weight-average molecular mass) and copolymers of dialkyldimethylammonium chloride and of acrylamide, sold under the name "Merquat 550".

[071] (11) quaternary diammonium polymers containing repeating units corresponding to the formula (VI):



wherein R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, and R<sub>16</sub> are independently chosen from C<sub>1</sub>-C<sub>20</sub> aliphatic, C<sub>1</sub>-C<sub>20</sub> alicyclic, C<sub>1</sub>-C<sub>20</sub> arylaliphatic groups, and lower hydroxyalkylaliphatic groups; or alternatively R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, and R<sub>16</sub>, together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally containing a second hetero atom other than nitrogen; or alternatively R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub>, and R<sub>16</sub> are independently chosen from linear and branched C<sub>1</sub>-C<sub>6</sub> alkyl groups substituted with at least one group chosen from nitriles, esters, acyls, amides, -CO-O-R<sub>17</sub>-D groups, and -CO-NH-R<sub>17</sub>-D groups, where R<sub>17</sub> is an alkylene and D is a quaternary ammonium group; A<sub>1</sub> and B<sub>1</sub> are independently chosen from linear and branched,

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$$-\text{[CH}_2\text{-CH(CH}_3\text{)-O]}_y\text{-CH}_2\text{-CH(CH}_3\text{)-}$$

representing a defined and unique degree of polymerization or any number ranging to 4 and representing an average degree of polymerization;

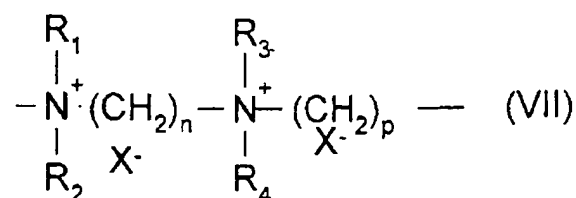
c) bis-primary diamine residues of formula:  $\text{-NH-Y-NH-}$ , where Y is

n from linear and branched hydrocarbon groups and  $-\text{CH}_2\text{CH}_2\text{S-S-CH}_2\text{CH}_2-$ ;

d) ureylene groups of formula: -NH-CO-NH-.

[074] These polymers generally have a number-average molecular mass ranging from about 1000 to about 100,000. Examples of these polymers of this type are described in U.S. Patent Nos. 2,273,780, 2,375,853, 2,388,614, 2,454,547, 3,206,462, 2,261,002, 2,271,378, 3,874,870, 4,001,432, 3,929,990, 3,966,904, 4,005,193, 4,025,617, 4,025,627, 4,025,653, 4,026,945, and 4,027,020, the disclosures of which relating to quaternary diammonium polymers are incorporated herein by reference.

[075] In one embodiment, the cationic conditioning polymers of family (11) consist of repeating units corresponding to the formula:



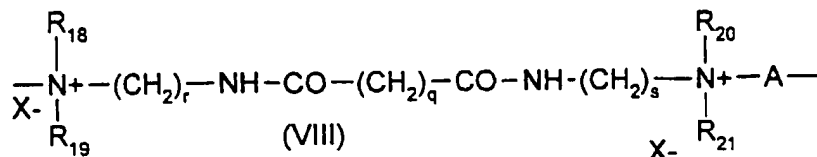
wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently chosen from C<sub>1</sub>-C<sub>4</sub> alkyl and C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical, n and p are integers independently ranging from about 2 to about 20, and X<sup>-</sup> is an anion chosen from inorganic and organic acids.

[076] In one embodiment, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are chosen from methyl groups; n = 3; p = 6; and X = Cl, which is known as Hexadimethrine chloride according to the INCI (CTFA) nomenclature.

[077] (12) polyquaternary ammonium polymers consisting of units of formula (VIII):

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wherein R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub>, and R<sub>21</sub> are independently chosen from hydrogen, methyl, ethyl, propyl, β-hydroxyethyl, β-hydroxypropyl, and -CH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>p</sub>OH groups, where p is an integer ranging from 0 to 6 with the proviso that R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub>, and R<sub>21</sub> are not simultaneously hydrogen; r and s are integers independently ranging from 1 to 6; q is an integer ranging from 0 to 34; X<sup>-</sup> is chosen from anions, such as halides; A is chosen from dihalide groups, such as -CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-.

[078] Such compounds are described in particular in patent application EP-A-122 324, the disclosure of which relating to polyquaternary ammonium polymers is incorporated herein by reference. Among these products, mention may be made, for example, of "Mirapol<sup>®</sup> A 15", "Mirapol<sup>®</sup> AD1", "Mirapol<sup>®</sup> AZ1" and "Mirapol<sup>®</sup> 175" sold by the company Miranol.

[079] (13) quaternary polymers of vinylpyrrolidone and of vinylimidazole, such as, for example, the products sold under the names Luviquat<sup>®</sup> TFC, FC 905, FC 550, and FC 370 by the company BASF.

[080] (14) polyamines such as Polyquart<sup>®</sup> H sold by Henkel under the reference name "Polyethylene glycol (15) tallow polyamine" in the CTFA dictionary.

[081] (15) non-crosslinked and crosslinked methacryloyloxy(C<sub>1</sub>-C<sub>4</sub>)alkyltri-(C<sub>1</sub>-C<sub>4</sub>)alkylammonium salt polymers such as the polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride, or by copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized with a methyl halide (such as chloride), the homo- or copolymerization

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being followed by crosslinking with a compound containing olefinic unsaturation, in particular methylenebisacrylamide. In one embodiment, a crosslinked acrylamide/methacryloyloxyethyl trimethylammonium chloride copolymer (20/80 by weight) in the form of a dispersion containing 50% by weight of the said copolymer in mineral oil is used. This dispersion is sold under the name "Salcare® SC 92" by the company Allied Colloids. In another embodiment, a crosslinked methacryloyloxyethyl trimethylammonium chloride homopolymer containing about 50% by weight of the homopolymer in mineral oil or in a liquid ester can also be used. These dispersions are sold under the names "Salcare® SC 95" and "Salcare® SC 96" by the company Allied Colloids.

[082] Other cationic conditioning polymers which can be used in the context of the invention are cationic proteins or cationic protein hydrolysates, polyalkyleneimines, in particular polyethyleneimines, polymers containing vinylpyridine or vinylpyridinium units, condensates of polyamines and of epichlorohydrin, quaternary polyureylenes and chitin derivatives.

[083] In one embodiment, the cationic conditioning polymers are chosen from quaternary cellulose ether derivatives such as the products sold under the name "JR 400" by the company Union Carbide Corporation; quarternized guar gum such such as the products sold under the name "Jaguar C 13 S" by the company Rhodia; cationic cyclopolymers, in particular the homopolymers or copolymers of dimethyldiallylammonium chloride, sold under the names "Merquat 100", "Merquat 550" and "Merquat S" by the company Calgon, quaternary polymers of vinylpyrrolidone and of vinylimidazole; non-crosslinked and crosslinked

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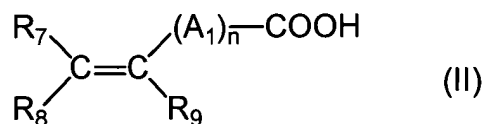
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methacryloyloxy(C<sub>1</sub>-C<sub>4</sub>)alkyltri(C<sub>1</sub>-C<sub>4</sub>)alkylammonium salt polymers such as the products sold under the name "Salcare SC 96" by the company NALCO; and mixtures thereof.

[084] According to the invention, the cationic conditioning polymer(s) can represent from about 0.001% to about 20% by weight, such as from about 0.01% to about 10% by weight, also such as from about 0.1% to about 3% by weight, relative to the total weight of the final composition.

[085] The anionic polymers, which can be used according to the present invention, are polymers comprising groups derived from carboxylic, sulfonic, and/or phosphoric acid and having a weight average molecular weight ranging from about 500 to about 5,000,000.

[086] (1) The carboxyl groups may be contributed by unsaturated mono- and dicarboxylic acid monomers such as those corresponding to the formula:



in which n is an integer ranging from 0 to 10; A<sub>1</sub> denotes a methylene group and when n is greater than 1, each A<sub>1</sub> is independently represented by -LCH<sub>2</sub>-, where L is chosen from a valency bond and heteroatoms, such as oxygen and sulfur; R<sub>7</sub> is chosen from hydrogen, phenyl groups, and benzyl groups; R<sub>8</sub> is chosen from hydrogen, lower alkyl groups, and carboxyl groups; and R<sub>9</sub> is chosen from hydrogen, lower alkyl groups, -CH<sub>2</sub>-COOH groups, phenyl groups, and benzyl groups.

[087] As defined herein, a lower alkyl group denotes a group having 1 to 4 carbon atoms, such as methyl and ethyl.

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[088] The anionic polymers comprising carboxyl groups according to the invention may be chosen from:

[089] A) Homopolymers and copolymers of (meth)acrylic acids or (meth)acrylic salts and in particular the products sold under the names Versicol E or K by the company Allied Colloid and Ultrahold by the company BASF, the copolymers of acrylic acid and of acrylamide sold in the form of their sodium salt under the names Reten 421, 423, or 425 by the company Hercules, and the sodium salts of polyhydroxycarboxylic acids.

[090] B) Copolymers of (meth)acrylic acid with a monoethylenic monomer, such as ethylene, styrene, vinyl esters, and (meth)acrylic acid esters, optionally grafted onto a polyalkylene glycol, such as polyethylene glycol, and optionally crosslinked. Such polymers are disclosed in particular in French Patent 1,222,944 and German Application 2,330,956, the disclosures of which relating to such copolymers are incorporated herein by reference. The copolymers of this type comprising, in their chain, an optionally N-alkylated and/or hydroxyalkylated acrylamide unit, such as disclosed in particular in Luxembourg Patent Applications 75370 and 75371, the disclosures of which relating to such copolymers are incorporated herein by reference, or sold under the name Quadramer by the company American Cyanamid. Mention may also be made of copolymers of acrylic acid and of C<sub>1</sub>-C<sub>4</sub> alkyl methacrylate and terpolymers of vinylpyrrolidone, of acrylic acid, and of C<sub>1</sub>-C<sub>20</sub> alkyl methacrylate for example lauryl methacrylate, such as Acrylidone LM available from the company ISP, and methacrylic acid/ethyl

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acrylate/tert-butyl acrylate terpolymers, such as the product sold under the name Luvimer 100 P by the company BASF.

[091] C) copolymers derived from crotonic acid, such as those comprising, in their chain, vinyl acetate or propionate units and optionally other monomers, such as (meth)allyl esters; vinyl ethers and vinyl esters of linear and branched saturated carboxylic acids comprising a long hydrocarbon chain, such as those comprising at least 5 carbon atoms, it optionally being possible for these polymers to be grafted and crosslinked; or alternatively vinyl and (meth)allyl esters of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid. Such polymers are disclosed, inter alia, in French Patents 1,222,944, 1,580,545, 2,265,782, 2,265,781, 1,564,110, and 2,439,798, the disclosures of which relating to copolymers of crotonic acid are incorporated herein by reference. Commercial products coming within this class are the Resins 28-29-30, 26-13-14, and 28-13-10 sold by the company National Starch.

[092] D) copolymers derived from C<sub>4</sub>-C<sub>8</sub> monounsaturated carboxylic acids or anhydrides chosen from:

- copolymers comprising units derived from (i) at least one monomer chosen from maleic, fumaric, and itaconic acids and anhydrides thereof and (ii) at least one monomer chosen from vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acids, and acrylic acid esters, the anhydride functional groups of these copolymers optionally being monoesterified or monoamidated. Such polymers are disclosed in particular in U.S. Patent Nos. 2,047,398, 2,723,248, and 2,102,112 and GB 839,805, the disclosures of which relating to such copolymers are

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incorporated herein by reference, and in particular those sold under the names Gantrez AN or ES by the company ISP.

- copolymers comprising units derived from (i) at least one monomer chosen from maleic, citraconic, and itaconic anhydrides and (ii) at least one monomer chosen from (meth)allyl esters, optionally comprising in their chain at least one unit derived from groups chosen from (meth)acrylamide,  $\alpha$ -olefin, (meth)acrylic ester, (meth)acrylic acid, and vinylpyrrolidone groups. The anhydride functional groups of these copolymers optionally are monoesterified or monoamidated.

[093] These polymers are, for example, disclosed in French Patents 2,350,384 and 2,357,241 the disclosures of which relating to such copolymers are incorporated herein by reference.

[094] E) polyacrylamides comprising carboxylate groups.

[095] (2) The anionic polymers comprising sulfonic groups may be chosen from polymers comprising units, such as those derived from vinylsulfonic, styrenesulfonic, naphthalenesulfonic, and acrylamidoalkylsulfonic acids and their derivatives. These polymers may be chosen from:

- salts of polyvinylsulfonic acid having a weight average molecular weight that ranges from about 1000 to about 100,000, as well as the copolymers derived from at least one unsaturated comonomer, such as (meth)acrylic acids, their esters, acrylamides, their derivatives, vinyl ethers, and vinylpyrrolidone;
- salts of polystyrenesulfonic acid, the sodium salts having a weight average molecular weight ranging from about 100,000 to about 500,000, which are sold respectively under the names Flexan 500 and Flexan 130 by National Starch.

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These compounds are disclosed in Patent FR 2,198,719, the disclosure of which relating to salts of polystyrenesulfonic acid is incorporated herein by reference;

- salts of polyacrylamidesulfonic acids, including those mentioned in U.S. Patent No. 4,128,631, the disclosure of which relating to salts of polyacrylamidesulfonic acid is incorporated herein by reference, and more particularly the polyacrylamidoethylpropanesulfonic acid sold under the name Cosmedia Polymer HSP 1180 by Henkel.

[096] In one embodiment, the anionic polymers are chosen from acrylic acid copolymers, such as the acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymer sold under the name Ultrahold Strong by the company BASF; copolymers derived from crotonic acid, such as the vinyl acetate/vinyl tert-butylbenzoate/crotonic acid terpolymers and the crotonic acid/vinyl acetate/vinyl neodecanoate terpolymers sold under the name Resin 28-29-30 by the company National Starch; polymers derived from at least one monomer chosen from maleic, fumaric, and itaconic acids and anhydrides thereof and also from at least one monomer chosen from vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid, and esters of acrylic acid, such as the monoesterified methyl vinyl ether/maleic anhydride copolymer sold under the name Gantrez ES 425 by the company ISP; copolymers of methacrylic acid and of methyl methacrylate sold under the name Eudragit L by the company Rohm Pharma; the copolymer of methacrylic acid and of ethyl acrylate sold under the name Luvimer MAEX or MAE by the company BASF; the vinyl acetate/crotonic acid copolymer sold under the name Luviset CA 66 by the company BASF; and the vinyl acetate/crotonic acid

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copolymer grafted by polyethylene glycol sold under the name Aristoflex A by the company BASF.

[097] In another embodiment, the anionic polymers are chosen from the monoesterified methyl vinyl ether/maleic anhydride copolymer sold under the name Gantrez ES 425 by the company ISP; the acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymer sold under the name Ultrahold Strong by the company BASF; the copolymers of methacrylic acid and of methyl methacrylate sold under the name Eudragit L by the company Rohm Pharma; the vinyl acetate/vinyl tert-butylbenzoate/crotonic acid terpolymers and the crotonic acid/vinyl acetate/vinyl neodecanoate terpolymers sold under the name Resin 28-29-30 by the company National Starch; the copolymer of methacrylic acid and of ethyl acrylate sold under the name Luvimer MAEX or MAE by the company BASF; and the vinyl-pyrrolidone/acrylic acid/lauryl methacrylate terpolymer sold under the name Acrylidone LM by the company ISP.

[098] The amphoteric polymers, which can be used in accordance with the invention, may be chosen from polymers comprising X and Y units, distributed randomly in the polymer chain, where the X unit is chosen from units derived from at least one monomer comprising at least one basic function, in particular a basic nitrogen atom, and where the Y unit is chosen from units derived from at least one acidic monomer comprising at least one group chosen from carboxyl groups and sulfo groups, or else where each X and Y unit is independently chosen from groups derived from zwitterionic carboxybetaine and sulfobetaine monomers. In another embodiment, the amphoteric polymers, which can be used in accordance with the

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invention, may be chosen from polymers comprising X and Y units, each X and Y unit is independently chosen from at least one cationic polymer chain comprising at least one group chosen from primary amine groups, secondary amine groups, tertiary amine groups, and quaternary amine groups, in which at least one of the amine groups comprises a group chosen from carboxyl and sulfo groups linked by way of a hydrocarbon group, or else the X and Y units, which may be different or identical, form part of a chain of at least one polymer comprising an  $\alpha,\beta$ -dicarboxy ethylene unit, wherein at least one of the carboxyl groups has been reacted with a polyamine comprising at least one group chosen from primary and secondary amine groups.

[099] In one embodiment, the amphoteric polymers corresponding to the definition given above are chosen from the following polymers:

[100] (1) polymers resulting from the copolymerization of a monomer derived from a vinyl compound carrying a carboxyl group, such as (meth)acrylic acids, maleic acids, and  $\alpha$ -chloracrylic acids, and of a basic monomer derived from a substituted vinyl compound comprising at least one basic atom, such as dialkylaminoalkyl (meth)acrylate and dialkylaminoalkyl (meth)acrylamide. Such compounds are disclosed in U.S. Patent No. 3,836,537, the disclosure of which relating to amphoteric polymers is incorporated herein by reference.

[101] (2) polymers comprising units derived from:

a) at least one monomer chosen from (meth)acrylamides substituted on the nitrogen with an alkyl group,

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b) at least one acidic comonomer comprising at least one reactive carboxylic group, and

c) at least one basic comonomer, such as esters comprising at least one substituent chosen from primary, secondary, tertiary, and quaternary amine substituents of (meth)acrylic acids, and the product of quaternization of dimethylaminoethyl methacrylate with dimethyl or diethyl sulfate.

[102] The at least one N-substituted (meth)acrylamide monomer recited in (a) is more particularly chosen from N-substituted (meth)acrylamides, wherein the alkyl groups comprise from 2 to 12 carbon atoms, such as N-ethylacrylamide, N-tert-butylacrylamide, N-tert-octylacrylamide, N-octylacrylamide, N-decylacrylamide, N-dodecylacrylamide, and the corresponding methacrylamides.

[103] The at least one acidic comonomer recited in (b) is more particularly chosen from (meth)acrylic acids, crotonic acids, itaconic acids, maleic acids, fumaric acids, C<sub>1</sub>-C<sub>4</sub> alkyl monoesters of maleic acid, C<sub>1</sub>-C<sub>4</sub> alkyl monoesters of fumaric acid, C<sub>1</sub>-C<sub>4</sub> alkyl monoesters of maleic anhydride, and C<sub>1</sub>-C<sub>4</sub> alkyl monoesters of fumaric anhydride.

[104] The at least one basic comonomer recited in (c) is more particularly chosen from aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl, and N-tert-butylaminoethyl methacrylates.

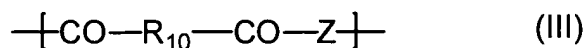
[105] In one embodiment, the amphoteric polymer is chosen from the copolymers for which the CTFA name (4th Ed., 1991) is octylacrylamide/ acrylates/ butylaminoethyl methacrylate copolymer, such as the products sold under the name Amphomer or Lovocryl 47 by the company National Starch.

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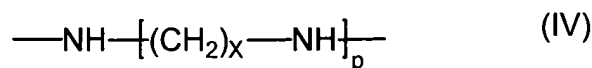
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[106] (3) crosslinked and alkylated polyamino amides partially or totally derived from polyamino amides of general formula:



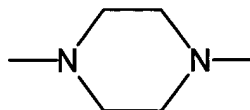
in which R<sub>10</sub> represents a divalent group derived either from a saturated dicarboxylic acid, from an aliphatic mono- or dicarboxylic acid comprising an ethylenic double bond, from an ester of a lower alkanol (having 1 to 6 carbon atoms) of these acids, or from a group derived from the addition of any one of the said acids with a bisprimary or bissecondary amine; and Z denotes a group of a bisprimary, mono- or bissecondary polyalkylenepolyamine and, for example, represents:

[107] a) in the proportions of from about 60 mol% to 100 mol%, the group:



where x=2 and p=2 or 3, or else x=3 and p=2 and where this group derives from diethylenetriamine, triethylenetetraamine, or dipropylenetriamine;

[108] b) in the proportions of from 0 mol% to about 40 mol%, the above group (IV), in which x=2 and p=1 and which derives from ethylenediamine, or the group derived from piperazine:



[109] c) in the proportions of from 0 mol% to about 20 mol%, the -NH-(CH<sub>2</sub>)<sub>6</sub>-NH- group derived from hexamethylenediamine, these polyamino amines being crosslinked by addition of a difunctional crosslinking agent chosen from epihalohydrines, diepoxides, dianhydrides and bis-unsaturated derivatives, using from about 0.025 mol to about 0.35 mol of crosslinking agent per amine group of the

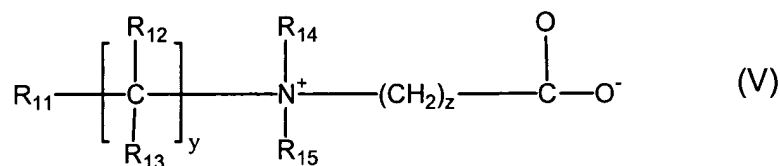
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polyamino amide and alkylated by the action of acrylic acid, chloroacetic acid or an alkane sultone, or salts thereof.

[110] In one embodiment, the saturated carboxylic acids are chosen from acids having 6 to 10 carbon atoms, such as adipic acid, 2,2,4-trimethyladipic acid, 2,4,4-trimethyladipic acid, terephthalic acid, and acids comprising an ethylenic double bond such as, for example, acrylic acid, methacrylic acid and itaconic acid.

[111] In one embodiment, the alkane sultones used in the alkylation are chosen from propane sultone and butane sultone and the salts of the alkylating agents are chosen from sodium and potassium salts.

[112] (4) polymers comprising zwitterionic units of formula:

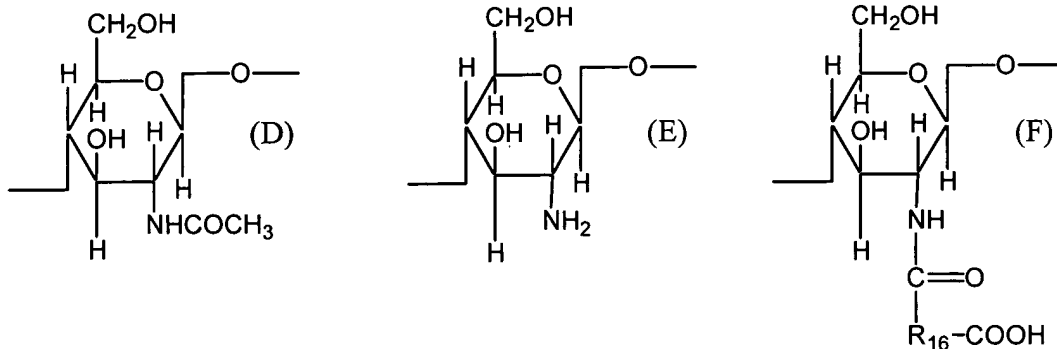


in which  $\text{R}_{11}$  is chosen from polymerizable unsaturated groups such as an (meth)acrylate and (meth)acrylamide groups;  $y$  and  $z$  are independently chosen from integers ranging from 1 to 3;  $\text{R}_{12}$  and  $\text{R}_{13}$  are independently chosen from hydrogen, methyl groups, ethyl groups, and propyl groups;  $\text{R}_{14}$  and  $\text{R}_{15}$  are independently chosen from hydrogen and alkyl groups, wherein the sum of the carbon atoms in  $\text{R}_{14}$  and  $\text{R}_{15}$  is less than or equal to 10.

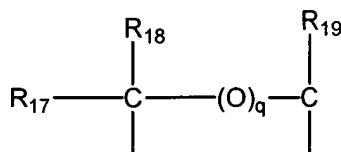
[113] The polymers comprising such units may further comprise units derived from non-zwitterionic monomers, such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, alkyl (meth)acrylates, (meth)acrylamides, and vinyl acetates.

[114] Mention may be made, by way of example, of the methyl methacrylate/ methyl dimethylcarboxymethylammonioethyl methacrylate copolymer, such as the product sold under the name Diaformer Z301 by the company Sandoz.

[115] (5) polymers derived from chitosan comprising monomer units corresponding to the following formulae:



the unit D being present in proportions ranging from 0% to about 30%, the unit E in proportions ranging from about 5% to about 50% and the unit F in proportions ranging from about 30% to about 90%, it being understood that, in this unit F,  $R_{16}$  represents a group of formula:



in which, if  $q=0$ ,  $R_{17}$ ,  $R_{18}$ , and  $R_{19}$ , which are identical or different, are chosen from hydrogen, methyl groups, hydroxyl groups, acetoxy groups, amino residues, monoalkylamine residues, and dialkylamine residues, optionally interrupted by one or more nitrogen atoms and/or optionally substituted by one or more amine, hydroxyl, carboxy, alkylthio, or sulfo groups, and alkylthio residues in which the alkyl group carries an amino residue, at least one of  $R_{17}$ ,  $R_{18}$ , and  $R_{19}$  being, in this case,

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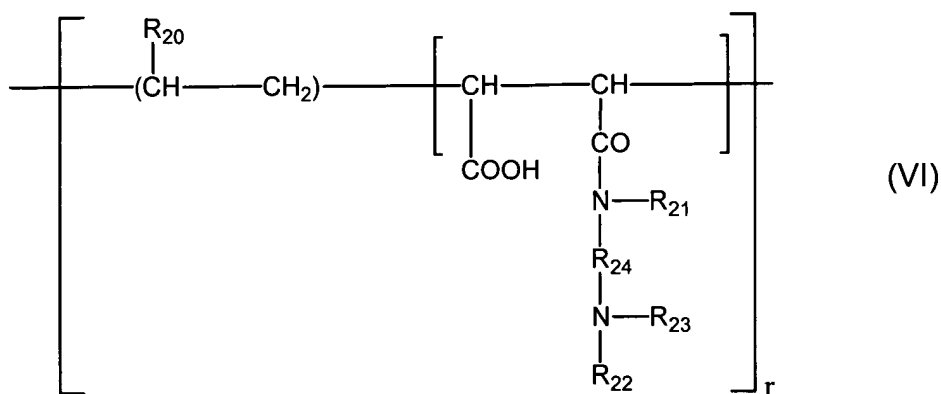
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hydrogen; or, if  $q=1$ ,  $R_{17}$ ,  $R_{18}$ , and  $R_{19}$  each represent hydrogen, and the salts formed by these compounds with bases or acids.

[116] (6) Polymers derived from the N-carboxyalkylation of chitosan, such as the N-(carboxymethyl)chitosan or the N-(carboxybutyl)chitosan sold under the name "Evalsan" by the company Jan Dekker.

[117] (7) Polymers corresponding to the general formula (VI), for example disclosed in French Patent 1,400,366, the disclosure of which relating to amphoteric polymers is incorporated herein by reference:



in which  $R_{20}$  is chosen from hydrogen,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{O}$ , and phenyl groups;  $R_{21}$  is chosen from hydrogen and lower alkyl groups such as methyl or ethyl;  $R_{22}$  is chosen from hydrogen and lower alkyl groups such as methyl or ethyl; and  $R_{23}$  is chosen from lower alkyl groups such as methyl or ethyl and groups corresponding to the formula:  $-R_{24}-\text{N}(\text{R}_{22})_2$ , where  $R_{24}$  is chosen from  $-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ , and  $-\text{CH}_2-\text{CH}(\text{CH}_3)-$  groups and  $R_{22}$  is the same as above, and the higher homologues of these groups comprising up to 6 carbon atoms.

[118] (8) Amphoteric polymers of the -D-X-D-X- type chosen from:

[119] a) polymers obtained by reaction of chloracetic acid or sodium chloracetate with compounds comprising at least one unit of formula:



where D denotes a group



and X denotes the symbol E or E'. E and E', which are identical or different, denote a divalent group chosen from straight- and branched-chain alkylene groups comprising up to 7 carbon atoms in the main chain, which is unsubstituted or substituted by hydroxyl groups and which can additionally comprise oxygen, nitrogen, or sulfur atoms or 1 to 3 aromatic and/or heterocyclic rings; the oxygen, nitrogen, and sulfur atoms being present in the form of ether, thioether, sulfoxide, sulfone, sulfonium, alkylamine or alkenylamine groups, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester, and/or urethane groups.

[120] b) Polymers of formula:



in which D denotes a group



and X denotes the symbol E or E', where X denotes E' at least once, E has the meaning indicated above, and E' is a divalent group chosen from straight- and branched-chain alkylene groups having up to 7 carbon atoms in the main chain, which is substituted or unsubstituted by one or more hydroxyl groups and which comprises one or more nitrogen atoms, the nitrogen atom being substituted by an alkyl chain optionally interrupted by an oxygen atom and necessarily comprising one

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or more carboxyl functional groups or one or more hydroxyl functional groups and wherein the polymer of formula VII' is betainized by reaction with chloracetic acid or sodium chloracetate.

[121] (9) (C<sub>1</sub>-C<sub>5</sub>)alkyl vinyl ether/maleic anhydride copolymers, which are partially modified by semiamidation with an N,N-dialkylaminoalkylamine, such as N,N-dimethylaminopropylamine, or by semiesterification with an N,N-dialkanolamine. These copolymers can also comprise other vinyl comonomers, such as vinylcaprolactam.

[122] In one embodiment, the amphoteric polymers according to the invention are chosen from family (3), such as the copolymers with the CTFA name (4<sup>th</sup> Ed. 1991) of octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer, such as the products sold under the names Amphomer, Amphomer LV 71, or Lovocryl 47 by the company National Starch, and family (4), such as the copolymer of methyl methacrylate/dimethyl carboxymethylammonio methyl ethylmethacrylate, sold, for example, under the name Diaformer Z301 by the company Sandoz.

[123] The nonionic polymers, which can be used according to the present invention, are chosen, for example, from:

- vinylpyrrolidone homopolymers;
- copolymers of vinylpyrrolidone and of vinyl acetate;
- polyalkyloxazolines, such as the polyethyloxazolines sold by the company Dow Chemical under the names PEOX 50,000, PEOX 200,000, and PEOX 500,000;

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- vinyl acetate homopolymers, such as the product sold under the name Appretan EM by the company Hoechst or the product sold under the name Rhodopas A 012 by the company Rhône-Poulenc;
- copolymers of vinyl acetate and of acrylic ester, such as the product sold under the name Rhodopas AD 310 by Rhône-Poulenc;
- copolymers of vinyl acetate and of ethylene, such as the product sold under the name Appretan TV by the company Hoechst;
- copolymers of vinyl acetate and of maleic ester, for example of dibutyl maleate, such as the product sold under the name Appretan MB Extra by the company Hoechst;
- copolymers of polyethylene and of maleic anhydride;
- alkyl acrylate homopolymers and alkyl methacrylate homopolymers, such as the product sold under the name Micropearl RQ 750 by the company Matsumoto or the product sold under the name Luhydran A 848 S by the company BASF;
- acrylic ester copolymers such as, for example, copolymers of alkyl (meth)acrylates, such as the products sold by the company Rohm & Haas under the names Primal AC-261 K and Eudragit NE 30 D, by the company BASF under the names Acronal 601, Luhydran LR 8833 or 8845, and by the company Hoechst under the names Appretan N 9213 or N 9212;
- copolymers of acrylonitrile and of a nonionic monomer chosen, for example, from butadiene and alkyl (meth)acrylates; mention may be made of the products sold under the names Nipol LX 531 B by the company Nippon Zeon or those sold under the name CJ 0601 B by the company Rohm & Haas;

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- polyurethanes, such as the products sold under the names Acrysol RM 1020 or Acrysol RM 2020 by the company Rohm & Haas, and the products Uraflex XP 401 UZ and Uraflex XP 402 UZ by the company DSM Resins;
- copolymers of alkyl acrylate and of urethane, such as the product 8538-33 by the company National Starch;
- polyamides, such as the product Estapor LO 11 sold by the company Rhône-Poulenc.
- nonionic guar gums that are chemically modified or unmodified.

[124] The unmodified nonionic guar gums are, for example, the products sold under the name Vidogum GH 175 by the company Unipeptine and under the name Jaguar C by the company Meyhall.

[125] The modified nonionic guar gums, which may be used according to the invention, are, for example, modified with C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl groups. Examples, which may be mentioned, are hydroxymethyl, hydroxyethyl, hydroxypropyl, and hydroxybutyl groups.

[126] These guar gums are well known in the prior art and may be prepared, for example, by reacting corresponding alkene oxides such as, for example, propylene oxides with guar gum so as to obtain a guar gum modified with hydroxypropyl groups.

[127] Such nonionic guar gums, optionally modified with hydroxyalkyl groups, are sold, for example, under the trade names Jaguar HP8, Jaguar HP60, Jaguar HP120, Jaguar DC 293, and Jaguar HP 105 by the company Meyhall and under the name Galactosol 4H4FD2 by the company Aqualon.

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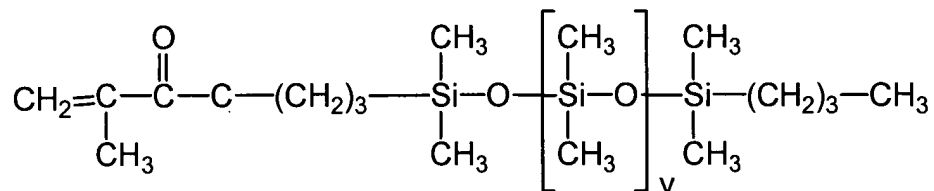
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[128] The alkyl groups in the nonionic polymers comprise from 1 to 6 carbon atoms, except where otherwise mentioned.

[129] According to the invention, it is also possible to use polymers of grafted silicone type comprising a polysiloxane portion and a portion comprising a non-silicone organic chain, one of the two portions constituting the main chain of the polymer and the other being grafted onto the main chain. These polymers are disclosed, for example, in EP-A-0,412,704, EP-A-0,412,707, EP-A-0,640,105, WO 95/00578, EP-A-0,582,152, and WO 93/23009 and U.S. Patent Nos. 4,693,935, 4,728,571, and 4,972,037, the disclosures of which relating to grafted silicone type polymers are incorporated herein by reference. These polymers are, for example, anionic or nonionic.

[130] Such polymers are, for example, copolymers which can be obtained by radical polymerization from the monomer mixture comprising:

- a) about 50% to about 90% by weight of tert-butyl acrylate;
- b) 0% to about 40% by weight of acrylic acid;
- c) about 5% to about 40% by weight of silicone macromer of formula:



where v is a number ranging from 5 to 700; the percentages by weight being calculated with respect to the total weight of the monomers.

[131] Other examples of grafted silicone polymers are, in particular, polydimethylsiloxanes (PDMSs) onto which are grafted, via a thiopropylene-type

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connecting chain, mixed polymer units of the poly(meth)acrylic acid type and of the poly(alkyl (meth)acrylate) type and polydimethylsiloxanes (PDMSs) onto which are grafted, via a thiopropylene-type connecting chain, polymer units of the poly(isobutyl (meth)acrylate) type.

[132] It is also possible to use, as polymers, functionalized or non-functionalized and silicone-comprising or non-silicone-comprising polyurethanes.

[133] Examples of useful polyurethanes include those disclosed in Patents EP 0,751,162, EP 0,637,600, FR 2,743,297, EP 0,648,485, EP 0,656,021, WO 94/03510, and EP 0,619,111, the disclosure of which relating to polyurethanes are incorporated herein by reference.

[134] In a further embodiment, the polymers may be used in solubilized form or may be in the form of dispersions of solid or liquid particles (latex or pseudo-latex).

[135] In one embodiment, the at least one constituent is chosen from anionic, amphoteric, nonionic, cationic surfactants, and mixtures thereof. In one embodiment, the at least one surfactant is present in an amount ranging from about 0.1% to about 60% by weight, such as from about 1% to about 40%, also as from about 5% to about 30%, relative to the total weight of the composition. In another embodiment, the composition is a shampoo, wherein the at least one surfactant is present in an amount ranging from about 5% to about 30% relative to the total weight of the composition. In yet another embodiment, the composition is a conditioner, wherein the at least one surfactant is present in an amount ranging from about 0.1% to about 15% relative to the total weight of the composition. In one

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embodiment, the composition is a conditioner, wherein the at least one surfactant is a cationic surfactant.

[136] Representative surfactants which are suitable for carrying out the present invention are, for example, the following:

[137] (i) Anionic surfactant(s):

[138] In the context of the present invention, the nature of the anionic surfactant is not of critical importance. Thus, examples of anionic surfactants, which can be used alone or in mixtures, include salts (such as alkaline salts, especially sodium salts, ammonium salts, amine salts, amino alcohol salts, and magnesium salts) of compounds (such as alkyl sulfates, alkyl ether sulfates, alkylamidoether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates, alkyl sulfonates, alkyl phosphates, alkylamide sulfonates, alkylaryl sulfonates,  $\alpha$ -olefin sulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfosuccinamates, alkyl sulfoacetates, alkyl ether phosphates, acyl sarcosinates, acyl isethionates, and N-acyltaurates). In one embodiment, the alkyl and acyl groups contain from about 8 to about 24 carbon atoms and the aryl groups are chosen from phenyl and benzyl groups.

[139] Among the anionic surfactants, which can also be used, mention may also be made of fatty acid salts (such as the salts of oleic, ricinoleic, palmitic, and stearic, coconut oil, and hydrogenated coconut oil acids); and acyl lactylates in which the acyl group contains 8 to 20 carbon atoms. Weakly anionic surfactants can also be used, such as alkyl-D-galactosiduronic acids and their salts, as well as polyoxyalkylenated ( $C_6$ - $C_{24}$ ) alkyl ether carboxylic acids, polyoxyalkylenated ( $C_6$ - $C_{24}$ )

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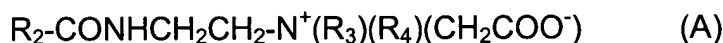
[142] With respect to the nonionic surfactants (see "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178), their nature is not a critical feature. Thus, examples of nonionic surfactants, which can be used alone or in mixtures, include fatty acids, alkylphenols,  $\alpha$ -diols, and alcohols; all of which have a fatty chain containing, for example, 8 to 18 carbon atoms and which have been polyethoxylated, polypropoxylated, and/or polyglycerolated, where the number of ethylene oxide or propylene oxide groups ranges from 2 to 50 and the number of glycerol groups ranges from 2 to 30. Mention may also be made of copolymers of ethylene oxide and of propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides (such as those with from 2 to 30 mols of ethylene oxide); polyglycerolated fatty amides containing on average 1 to 5, such as from 1.5 to 4 glycerol groups; polyethoxylated fatty amines (such as those having 2 to 30 mols of ethylene oxide); oxyethylenated fatty acid esters of sorbitan having from 2 to 30 mols of ethylene oxide; fatty acid esters of sucrose; fatty acid esters of polyethylene glycol; alkylpolyglycosides; N-alkylglucamine derivatives; and amine

oxides such as (C<sub>10</sub>-C<sub>14</sub>)alkylamine oxides and N-acylaminopropylmorpholine oxides. In one embodiment, the nonionic surfactants are chosen from alkylpolyglycosides.

[143] (iii) Amphoteric surfactant(s):

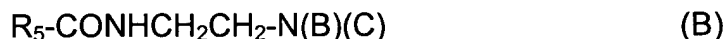
[144] The amphoteric surfactants, whose nature is not a critical feature, can be chosen from, for example, aliphatic secondary and tertiary amine derivatives in which the aliphatic radical is chosen from linear and branched chains containing 8 to 22 carbon atoms and containing at least one water-soluble anionic group (for example carboxylate, sulfonate, sulfate, phosphate, and phosphonate groups). Suitable examples include (C<sub>8</sub>-C<sub>20</sub>)alkylbetaines, sulfobetaines, (C<sub>8</sub>-C<sub>20</sub>)alkylamido (C<sub>1</sub>-C<sub>6</sub>)alkylbetaines, and (C<sub>8</sub>-C<sub>20</sub>)alkylamido(C<sub>1</sub>-C<sub>6</sub>)alkylsulfobetaines.

[145] Among the amine derivatives, mention may be made of the products having the formulae (A) and (B):



wherein R<sub>2</sub> is chosen from alkyl groups derived from an acid R<sub>2</sub>-COOH present in hydrolysed coconut oil, heptyl, nonyl, and undecyl groups, R<sub>3</sub> is chosen from β-hydroxyethyl groups, and R<sub>4</sub> is chosen from carboxymethyl groups;

and



wherein B is chosen from -CH<sub>2</sub>CH<sub>2</sub>OX', C is chosen from -(CH<sub>2</sub>)<sub>z</sub>-Y', with z = 1 or 2; X' is chosen from -CH<sub>2</sub>CH<sub>2</sub>-COOH groups and hydrogen; Y' is chosen from -COOH and -CH<sub>2</sub>-CHOH-SO<sub>3</sub>H groups; R<sub>5</sub> is chosen from alkyl radicals of an acid R<sub>9</sub>-COOH present in coconut oil and in hydrolysed linseed oil, alkyl radicals (such as C<sub>7</sub>, C<sub>9</sub>,

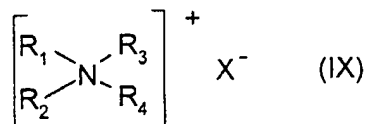
C<sub>11</sub>, and C<sub>13</sub> alkyl radicals), and C<sub>17</sub> alkyl radicals (such as the iso form and unsaturated C<sub>17</sub> radicals).

[146] These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, disodium capryloamphodipropionate, lauroamphodipropionic acid, and cocoamphodipropionic acid. A useful example may be the cocoamphodiacetate sold under the trade name Miranol C2M concentrate by the company Rhône-Poulenc.

[147] (iv) Cationic surfactant(s):

[148] The cationic surfactants may be chosen from:

[149] A) the quaternary ammonium salts of formula (IX) below:



wherein X<sup>-</sup> is an anion chosen from halides (such as chloride, bromide, and iodide) and (C<sub>2</sub>-C<sub>6</sub>)alkyl sulfates (such as methyl sulfates), phosphates, alkyl and alkylaryl sulfonates, anions derived from organic acids (such as acetate and lactate), and either:

[150] i) R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are independently chosen from

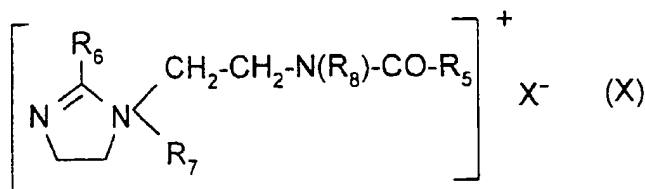
linear and branched aliphatic groups containing from 1 to 4 carbon atoms and aromatic groups (such as aryls and alkylaryls). The aliphatic groups may comprise hetero atoms such as, for example, oxygen, nitrogen, and sulfur, and halogens. The aliphatic groups may be chosen, for example, from alkyl, alkoxy, and alkylamide

groups.  $R_4$  may be chosen from linear and branched alkyl groups containing from 12 to 30 carbon atoms. In one embodiment the cationic surfactant is chosen from behenyltrimethylammonium salts (for example chloride); or

[151] ii)  $R_1$  and  $R_2$  are independently chosen from linear and branched aliphatic groups containing from 1 to 4 carbon atoms and aromatic groups including aryls and alkylaryls. The aliphatic groups may comprise one or more halogens and hetero atoms such as, for example, oxygen, nitrogen, and sulfur. The aliphatic groups may be chosen, for example, from alkyl, alkoxy, alkylamide, and hydroxyalkyl groups containing from about 1 to 4 carbon atoms.  $R_3$  and  $R_4$  are independently chosen from linear and branched alkyl groups containing from 12 to 30 carbon atoms, the said groups may comprise at least one function from esters and amide functions. In one embodiment,  $R_3$  and  $R_4$  may be chosen from  $(C_{12}-C_{22})$ alkylamido $(C_2-C_6)$ alkyl and  $(C_{12}-C_{22})$ alkylacetate groups.

[152] In one embodiment, the cationic surfactant is chosen from stearamidopropyldimethyl(myristyl acetate)ammonium salts (for example chloride). In another embodiment, the cationic surfactant is chosen from palmitamidopropyl trimonium chloride, which is sold under the name Varisoft PTC by Degussa Goldschmidt;

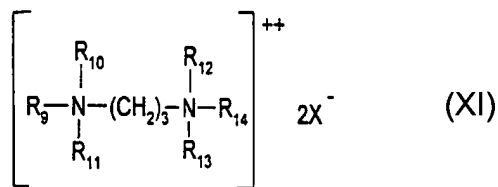
[153] B) the quaternary ammonium salts of imidazolinium, such as, for example, that of formula (X):





wherein R<sub>5</sub> is chosen from alkenyl and alkyl groups containing from 8 to 30 carbon atoms, such as, for example, fatty acid derivatives of tallow; R<sub>6</sub> is chosen from hydrogen, and alkenyl and alkyl groups containing from 8 to 30 carbon atoms; R<sub>7</sub> is chosen from C<sub>1</sub>-C<sub>4</sub> alkyl groups; R<sub>8</sub> is chosen from hydrogen and C<sub>1</sub>-C<sub>4</sub> alkyl groups; and X<sup>-</sup> is an anion chosen from halides, phosphates, acetates, lactates, alkyl sulfates, alkyl sulfonates, and alkylaryl sulfonates. In one embodiment, R<sub>5</sub> and R<sub>6</sub> are independently chosen from alkenyl and alkyl groups containing from 12 to 21 carbon atoms, such as, for example, fatty acid derivatives of tallow; R<sub>7</sub> is a methyl group; and R<sub>8</sub> is hydrogen. Examples include Quaternium-27 (CTFA 1997) and Quaternium-83 (CTFA 1997), which are sold under the names "Rewoquat" W75, W90, W75PG, and W75HPG by the company Witco;

[154] C) the diquaternary ammonium salts of formula (XI):

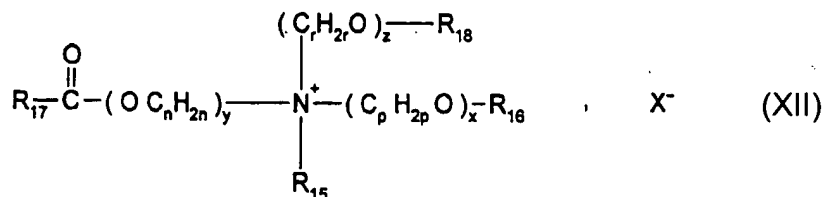


wherein R<sub>9</sub> is chosen from aliphatic groups containing from about 16 to about 30 carbon atoms; R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, and R<sub>14</sub> are independently chosen from hydrogen and alkyl groups containing from 1 to 4 carbon atoms; and X<sup>-</sup> is an anion chosen from halides, acetates, phosphates, nitrates, and methyl sulfates. Such diquaternary ammonium salts include propanetallowdiammonium dichloride; and

[155] D) the quaternary ammonium salts containing at least one ester function, of formula (XII) below:

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wherein R<sub>15</sub> is chosen from C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl, and dihydroxyalkyl groups; R<sub>16</sub> is chosen from R<sub>19</sub>-CO-, linear and branched, saturated and unsaturated C<sub>1</sub>-C<sub>22</sub> hydrocarbon-based groups R<sub>20</sub>, and hydrogen; R<sub>18</sub> is chosen from R<sub>21</sub>-CO-, linear and branched, saturated and unsaturated C<sub>1</sub>-C<sub>6</sub> hydrocarbon-based groups R<sub>22</sub>, and hydrogen; R<sub>17</sub>, R<sub>19</sub>, and R<sub>21</sub> are independently chosen from linear and branched, saturated and unsaturated C<sub>7</sub>-C<sub>21</sub> hydrocarbon-based groups; n, p, and r are integers independently ranging from 2 to 6; y is an integer ranging from 1 to 10; x and z are integers independently ranging from 0 to 10; X<sup>-</sup> is chosen from simple and complex, organic and inorganic anions; with the proviso that the sum x + y + z ranges from 1 to 15, that when x is 0, then R<sub>16</sub> denotes R<sub>20</sub>, and that when z is 0, then R<sub>18</sub> denotes R<sub>22</sub>.

[156] In one embodiment, R<sub>15</sub> is chosen from methyl and ethyl groups; x and y are equal to 1; z is equal to 0 or 1; n, p, and r are equal to 2; R<sub>16</sub> is chosen from R<sub>19</sub>-CO-, methyl, ethyl, and C<sub>14</sub>-C<sub>22</sub> hydrocarbon-based groups, and hydrogen; R<sub>17</sub>, R<sub>19</sub>, and R<sub>21</sub> are independently chosen from linear and branched, saturated and unsaturated C<sub>7</sub>-C<sub>21</sub> hydrocarbon-based groups; R<sub>18</sub> is chosen from R<sub>21</sub>-CO- and hydrogen.

[157] Examples include compounds sold under the names Dehyquat by the company Henkel, Stepanquat by the company Stepan, Noxamium by the company Ceca, and Rewoquat WE 18 by the company Rewo-Witco.

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[158] In one embodiment, the cationic surfactants is chosen from behenyltrimethylammonium chloride and stearamidopropylmethyl(myristyl acetate)ammonium chloride, sold under the name "Ceraphyl 70" by the company Van Dyk, and Quaternium-27 or Quaternium-83 sold by the company Witco.

[159] In the compositions in accordance with the invention, mixtures of surfactants may be utilized. For example, mixtures of anionic surfactants and mixtures of anionic surfactants with amphoteric and/or nonionic surfactants are possible.

[160] In one embodiment, a mixture comprising at least one anionic surfactant and at least one amphoteric surfactant is chosen. The at least one anionic surfactant may be chosen from, for example, sodium (C<sub>12</sub>-C<sub>14</sub>)alkyl sulfates, triethanolamine (C<sub>12</sub>-C<sub>14</sub>)alkyl sulfates, ammonium (C<sub>12</sub>-C<sub>14</sub>)alkyl sulfates, sodium (C<sub>12</sub>-C<sub>14</sub>)alkyl ether sulfates oxyethylenated with 2.2 mols of ethylene oxide, triethanolamine (C<sub>12</sub>-C<sub>14</sub>)alkyl ether sulfates oxyethylenated with 2.2 mols of ethylene oxide, ammonium (C<sub>12</sub>-C<sub>14</sub>)alkyl ether sulfates oxyethylenated with 2.2 mols of ethylene oxide, sodium cocoyl isethionates, and sodium (C<sub>14</sub>-C<sub>16</sub>)- $\alpha$ -olefin sulfonates. The at least one amphoteric surfactant may be chosen from, for example, amine derivatives known as disodium cocoamphodipropionates and sodium cocoamphopropionates, such as those sold by the company Rhône-Poulenc under the trade name "Miranol C2M Conc." as an aqueous solution containing 38% active material, or under the name Miranol C32, and amphoteric surfactants of the zwitterionic type, including alkylbetaines, such as the cocobetaine sold under the name "Dehyton AB 30" as an aqueous solution containing 32% AM, by the company

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Henkel. In one embodiment, the mixture comprises cocobetaine and sodium lauryl ether sulfate.

[161] The composition according to the invention may be vaporizable, for example by a pump, or may be a pressurized aerosol composition. It may be vaporizable by a dispensing valve controlled by a dispensing head, which in turn comprises a nozzle, which vaporizes the aerosol composition. A vaporizable composition according to the invention comprises an appropriate solvent.

Advantageously, the appropriate solvent comprises at least one solvent chosen from water and lower alcohols. In accordance with the invention, the term lower alcohol means a C<sub>1</sub> to C<sub>4</sub> aliphatic alcohol, such as ethanol.

[162] When the vaporizable composition according to the invention is an aerosol composition, it additionally comprises an appropriate amount of propellant. The propellant comprises compressed or liquefied gases, which are normally employed for the preparation of aerosol compositions. Suitable gasses include compressed air, carbon dioxide, nitrogen, and gases, which may be soluble in the composition, such as dimethyl ether, fluorinated or non-fluorinated hydrocarbons, and mixtures thereof.

[163] The present invention additionally provides an aerosol device comprising a vessel comprising an aerosol composition, which comprises a liquid phase (or juice) comprising at least one reshapable hair styling material, as described above, in an appropriate medium and a propellant, and a dispenser, such as a dispensing valve, for dispensing said aerosol composition from the vessel.

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[167] Where the composition is in the form of a lotion, for example, the *in vivo* test proceeds as follows. The hair of the model is washed and then divided into two symmetrical portions, the right and the left sides. The composition is applied to one side of the head of the model and then rinsed, while a reference composition is applied to the other side of the head. The reference composition may, for example, be chosen from water, an existing commercial product, or another composition under study. The hairdresser dries and styles both sides of the head. The two sides of the head are separately evaluated for the styling effect, the cosmetic properties, and the reshapable effect. For example, once dried, the hair is brushed in different directions to remove the original styling. The hair is then brushed to restore the original styling. The process of removing the styling, restoring the styling, and evaluating the success of restoring the styling is repeated at least one more time to determine whether the composition is a reshapable hair styling composition. A

reshapable hair styling composition permits (1) the original hair styling to be restored after brushing and (2) the creation of a new hair styling after brushing, which may also be restored after brushing. If the composition to be evaluated is in another form, such as a shampoo or conditioner, the *in vivo* test can be appropriately modified by one skilled in the art.

[168] It is understood that the person skilled in the art would recognize that not all formulations would provide reshapable effect for all hair types during *in vivo* testing and will know how to formulate and evaluate reshapable hair styling compositions in view of the various hair parameters, such as length (short versus long), diameter (thin versus thick), structure (curly versus straight), condition (oily, dry, or normal); and whether the hair is colored, bleached, permed, or straightened. Thus, *in vivo* testing may require testing on 10-20 different individuals.

[169] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should be construed in light of the number of significant digits and ordinary rounding approaches.

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[170] Any measured numerical value inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[171] EXAMPLES:

[172] Hair compositions according to the invention were produced with different (meth)acrylic emulsions.

1) Preparation of the acrylic emulsions:

[173] Example 1:

A mixture of 300 grams 2-ethyl hexyl acrylate (2-EHA), 175 grams n-butyl acrylate (BA), and 25 grams 2-hydroxy ethyl methacrylate (HEMA) was prepared yielding 500 grams of a monomer solution containing 60/35/5 parts 2-EHA/BA/HEMA. Of the total monomer solution, 50 grams was charged into a two liter split resin flask along with 380 grams of deionized water and 0.5 gram of RHODACAL DS-10 (sodium dodecyl benzene sulfonate surfactant commercially available from Rhône-Poulenc). The head was placed on the flask and a thermocouple, nitrogen inlet, and mechanical stirrer attached. The contents were heated with infra red lamps to about 60 °C while stirring at 350 rpm. A solution of 1 gram potassium persulfate initiator in 20 grams deionized water was charged, the flask sealed, and a vacuum pulled on the flask four times, breaking it each time with nitrogen. The flask was held at 60 °C for 20 minutes, then heated to 80 °C over 10 minutes to yield a seed polymer. A pre-emulsion of the remaining 450 grams of the monomer solution was prepared by charging a solution of 4.5 grams of sodium dodecyl benzene sulfonate in 211 grams of deionized water to it and stirring under

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nitrogen. This pre-emulsion was added dropwise to the two liter split resin flask containing the seed polymer at a rate of 6 grams per minute. The addition took almost 2 hours. After the addition, the stirring rate was reduced to 200 rpm and the reaction held at 80 °C for two hours, then the resulting latex was filtered through doubled over cheesecloth into a jar. Low levels of coagulum were noted around the thermocouple and stirring paddle.

[174] Prophetic Example 2:

A mixture of 300 grams (2-EHA), 100 grams iso-butyl acrylate (IBA), 75 grams (BA), and 25 grams (HEMA) is prepared yielding 500 grams of a monomer solution containing 60/20/15/5 parts 2-EHA/IBA/BA/HEMA. Of the total monomer solution, 50 grams is charged into a two liter split resin flask along with 380 grams of deionized water and 0.5 gram of RHODACAL DS-10 (sodium dodecyl benzene sulfonate surfactant commercially available from Rhône-Poulenc). The head is placed on the flask and a thermocouple, nitrogen inlet, and mechanical stirrer are attached. The contents are heated with infra red lamps to about 60 °C while stirring at 350 rpm. A solution of 1 gram potassium persulfate initiator in 20 grams deionized water is charged, the flask is sealed, and a vacuum is pulled on the flask four times, breaking it each time with nitrogen. The flask is held at 60 °C for 20 minutes, then is heated to 80 °C over 10 minutes to yield a seed polymer. A pre-emulsion of the remaining 450 grams of the monomer solution is prepared by charging a solution of 4.5 grams of sodium dodecyl benzene sulfonate in 211 grams of deionized water to it and stirring under nitrogen. This pre-emulsion is added dropwise to the two liter split resin flask containing the seed polymer at a rate of 6

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grams per minute. The addition takes almost 2 hours. After the addition, the stirring rate is reduced to 200 rpm and the reaction is to be held at 80 °C for two hours, then the resulting latex will be filtered through doubled over cheesecloth into a jar.

[175] Prophetic Example 3:

A mixture of 300 grams (IBA), 150 grams (BA), and 50 grams 2-hydroxy ethyl acrylate (HEA) is prepared yielding 500 grams of a monomer solution containing 60/3/10 parts IBA/BA/HEA. Of the total monomer solution, 50 grams is charged into a two liter split resin flask along with 380 grams of deionized water and 0.5 gram of RHODACAL DS-10 (sodium dodecyl benzene sulfonate surfactant commercially available from Rhône-Poulenc). The head is placed on the flask and a thermocouple, nitrogen inlet, and mechanical stirrer are attached. The contents are heated with infra red lamps to about 60 °C while stirring at 350 rpm. A solution of 1 gram potassium persulfate initiator in 20 grams deionized water is charged, the flask is sealed, and a vacuum is pulled on the flask four times, breaking it each time with nitrogen. The flask is held at 60 °C for 20 minutes, then is heated to 80 °C over 10 minutes to yield a seed polymer. A pre-emulsion of the remaining 450 grams of the monomer solution is prepared by charging a solution of 4.5 grams of sodium dodecyl benzene sulfonate in 211 grams of deionized water to it and stirring under nitrogen. This pre-emulsion is added dropwise to the two liter split resin flask containing the seed polymer at a rate of 6 grams per minute. The addition takes almost 2 hours. After the addition, the stirring rate is reduced to 200 rpm and the reaction is to be held at 80 °C for two hours, then the resulting latex will be filtered through doubled over cheesecloth into a jar.

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[176] Prophetic Example 4:

A mixture of 300 grams 2-carboxyethyl acrylates (2-CEA), 175 grams (BA), and 25 grams (HEMA) is prepared yielding 500 grams of a monomer solution containing 60/35/5 parts 2-CEA/BA/HEMA. Of the total monomer solution, 50 grams is charged into a two liter split resin flask along with 380 grams of deionized water and 0.5 gram of RHODACAL DS-10 (sodium dodecyl benzene sulfonate surfactant commercially available from Rhône-Poulenc). The head is placed on the flask and a thermocouple, nitrogen inlet, and mechanical stirrer are attached. The contents are heated with infra red lamps to about 60 °C while stirring at 350 rpm. A solution of 1 gram potassium persulfate initiator in 20 grams deionized water is charged, the flask is sealed, and a vacuum is pulled on the flask four times, breaking it each time with nitrogen. The flask is held at 60 °C for 20 minutes, then is heated to 80 °C over 10 minutes to yield a seed polymer. A pre-emulsion of the remaining 450 grams of the monomer solution is prepared by charging a solution of 4.5 grams of sodium dodecyl benzene sulfonate in 211 grams of deionized water to it and stirring under nitrogen. This pre-emulsion is added dropwise to the two liter split resin flask containing the seed polymer at a rate of 6 grams per minute. The addition takes almost 2 hours. After the addition, the stirring rate is reduced to 200 rpm and the reaction is to be held at 80 °C for two hours, then the resulting latex will be filtered through doubled over cheesecloth into a jar.

[177] Prophetic Example 5:

A mixture of 300 grams styrene (S), 175 grams (BA), and 25 grams (HEMA) is prepared yielding 500 grams of a monomer solution containing 60/35/5 parts

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S/BA/HEMA. Of the total monomer solution, 50 grams is charged into a two liter split resin flask along with 380 grams of deionized water and 0.5 gram of RHODACAL DS-10 (sodium dodecyl benzene sulfonate surfactant commercially available from Rhône-Poulenc). The head is placed on the flask and a thermocouple, nitrogen inlet, and mechanical stirrer are attached. The contents are heated with infra red lamps to about 60 °C while stirring at 350 rpm. A solution of 1 gram potassium persulfate initiator in 20 grams deionized water is charged, the flask is sealed, and a vacuum is pulled on the flask four times, breaking it each time with nitrogen. The flask is held at 60 °C for 20 minutes, then is heated to 80 °C over 10 minutes to yield a seed polymer. A pre-emulsion of the remaining 450 grams of the monomer solution is prepared by charging a solution of 4.5 grams of sodium dodecyl benzene sulfonate in 211 grams of deionized water to it and stirring under nitrogen. This pre-emulsion is added dropwise to the two liter split resin flask containing the seed polymer at a rate of 6 grams per minute. The addition takes almost 2 hours. After the addition, the stirring rate is reduced to 200 rpm and the reaction is to be held at 80 °C for two hours, then the resulting latex will be filtered through doubled over cheesecloth into a jar.

[178] Prophetic Example 6:

A 50/50 mixture of the emulsion from Example 1 and a dispersion comprising AQ 1350 by the Eastman Chemical Co. as disclosed in WO 98/38969 can be made.

[179] Prophetic Example 7:

A 25/75 mixture of the emulsion from Example 1 and the emulsion from Example 2 can be made.

2) Preparation of the hair styling compositions:

[180] Five hair styling compositions in accordance with the invention in the form of a shampoo were prepared using the components and amounts in weight percent listed hereafter. The testing was conducted on several models with one part of the head receiving one composition and the other side of the head receiving the other composition.

[181] Formulation A:

Example 1	3.75 % active material
Merquat 550 by Calgon	0.28 % active material
Sodium lauryl ether sulfate (2.2 OE)	9.0 % active material
Cocobetaine	5.25% active material
Varisoft PATC by Degussa Goldschmidt	0.7% active material
Perfume, preservative	qs
Water	qsp 100 %

[182] Formulation B:

Example 1	3.75 % active material
Merquat 100 by Calgon	0.28 % active material
Sodium lauryl ether sulfate (2.2 OE)	9.0 % active material
Cocobetaine	5.25% active material
Varisoft PATC by Degussa Goldschmidt	0.7% active material
Perfume, preservative	qs
Water	qsp 100 %

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Formulation B imparts good hairstyling with good cosmetic properties and a reshapable effect comparable to Formulation A.

[183] Additional formulations were manufactured.

[184] Formulation C:

Example 1	2 % active material
Merquat 550	0.15% active material
Sodium lauryl ether sulfate (2.2 OE)	9.0 % active material
Cocobetaine	5.25% active material
Perfume, preservative	qs
Water	qsp 100 %

Formulation C imparted a reshapable effect.

[185] Formulation D:

Example 1	5 % active material
Merquat 550	0.28 % active material
Sodium lauryl ether sulfate (2.2 OE)	9.0 % active material
Cocobetaine	5.25% active material
Varisoft PATC by Degussa Goldschmidt	0.7% active material
Perfume, preservative	qs
Water	qsp 100 %

Formulation D imparted a reshapable effect.

[186] Formulation E:

Example 1	0.3 % active material
Salcare SC 95 by Allied Colloids	1.0 % active material

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Water

qsp 100 %

Formulation E imparted a reshapable effect.

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